A Dinucleating Bis(dimethylcyclam) Ligand and Its Dinickel(II) and Dizinc(II) Complexes with the Face-to-Face Ring Arrangement

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The chemistry of metal complexes with cyclam or related tetraaza macrocyclic ligands has been extensively developed.[1] The preparation of dinucleating ligands with two such macrocyclic rings was also attempted, aiming at the cooperative interaction of two metallic sites in the metal complexes.[2-4] To our knowledge, however, no one has succeeded in synthesizing a metal complex with the cofacial ring arrangement, except for the face-to-face diporphyrin complexes.[5] In this paper, we report a new dinucleating ligand comprised of two dimethylcyclams bridged at the carbon center with an *ortho*-xylylene group and its bridged dinickel(II) and dizinc(II) complexes with a cofacial ring arrangement.

The dinucleating ligand, α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene (L) and its dinickel(II) and dizinc(II) complexes were successfully prepared according to Scheme I. It is well-known that the charge-delocalized six-membered chelate ring of the starting nickel(II) complex **1** exhibits marked nucleophillic character at the central carbon atom.[6] When 2 mol of **1** was allowed to react with α,α'-dihaloxylene (X = Cl, Br), the expected nucleophillic attack took place smoothly[7] to give the dinickel complex (**2**) in 60–80% yield. The imine bonds in **2** were reduced by $NaBH_4$. Although the reduction process can produce a mixture of diastereomers according to the newly generated asymmetric centers, the main (more than 80%) reduction product was a compound with C* meso-form in each cyclam ring (vide infra). $[Ni_2(\mu\text{-}Br)Br_2(L)]Br\cdot H_2O$ (**3**)[8] is formed as a good quality red orange crystalline compound and was obtained in a 60–70% yield from **2**. Other compounds, the free ligand (**4**),[9] $[Zn_2(L)](ClO_4)_4$ (**5**),[10] and $[Zn_2(\mu\text{-}CO_3)(L)](ClO_4)_2\cdot 2H_2O$ (**6**),[11] were derived from **3**. Complex **6** has been obtained from slow crystallization (a few weeks) of **5** in ca. 0.1 M NaOH aqueous solution (M = mol dm^{-3}).[12] That is, $[Zn_2(L)](ClO_4)_4$ (**5**) spontaneously takes up atmospheric CO_2 as CO_3^{2-} in basic aqueous solution.[13]

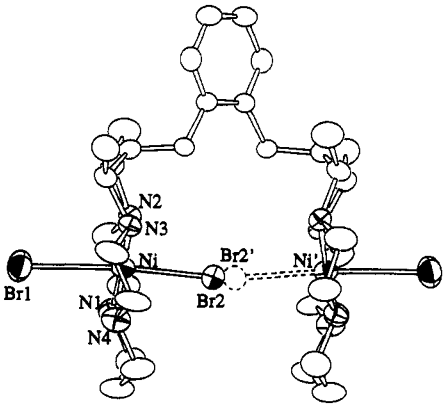

Figure 1. ORTEP drawing of $[Ni_2(\mu\text{-}Br)Br_2(L)]^+$ in **3**. The dotted atom and bond show the disorder of the Br(2) atom (see text). Distances (Å) and angles (deg): Ni–Br(1) = 2.881(1), Ni–Br(2) = 2.573(2), Ni–Br(2′) = 3.264(2), Ni–Ni′ = 5.802(2), Ni–N = 2.004(7)–2.024(6); Br(1)–Ni–Br(2) = 172.45(8), Br(1)–Ni–N = 82.0(2)–95.4(2), Br(2)–Ni–N = 84.8(2)–94.9(2).

Figures 1 and 2 show X-ray structures of the complex ions in **3**[14] and **6**,[12] respectively. In both structures, two cyclam rings are arranged in a typical face-to-face manner as expected,[15] and the bimetallic site is connected by the bridging ligand, Br^- in **3**

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(6) Martin, J. G.; Cummings, S. C. *Inorg. Chem.* **1973**, *12*, 1477–1482.

(7) Similar condensation reactions between complex **1** and tere- and isophthaloyl dichloride have been reported.[3b]

(8) A single crystal transmittance absorption spectrum of **3** shows weak absorption bands around 660 nm in addition to the strong broad band centered at 480 nm.

(9) Recrystallization of **4** (=L) from CH_3CN gave colorless needles. Anal. Calcd for $L\cdot CH_3CN\cdot 0.5H_2O$, $N_9C_{34}H_{66}O_{0.5}$: C, 67.06; H, 10.92; N, 20.70. Found: C, 67.24; H, 10.90; N, 20.55. ^{13}C NMR data in $CDCl_3$: 1.9 ($\mathit{C}H_3CN$), 19.9 ($\mathit{C}H_3$ in L), 26.7, 29.5, 47.4, 50.3 ($CH_2\text{–}\mathit{C}H\text{–}(CH(CH_3))_2$), 51.1, 51.3, 61.3 ($NH\text{–}\mathit{C}H(CH_3)\text{–}$), 116.4 ($CH_3\mathit{C}N$), 125.3 (benzene ring), 129.9 (benzene ring), 141.1 (benzene ring) ppm.

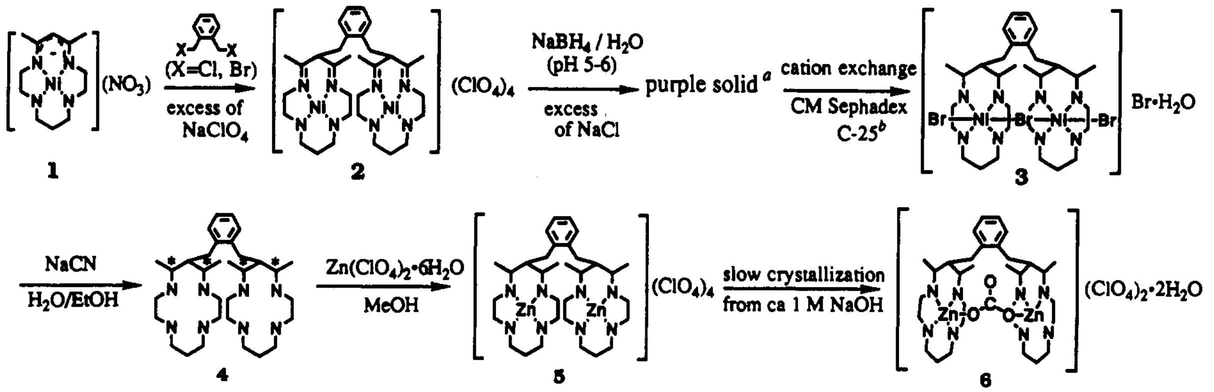
(10) Anal. Calcd for $[Zn_2(L)](ClO_4)_4$ (**5**), $Zn_2N_8C_{32}H_{62}Cl_4O_{16}$: C, 35.34; H, 5.75; N, 10.30. Found: C, 35.34; H, 5.73; N, 10.45.

(11) Compound **6** was also obtained by slow crystallization of $[Zn_2(L)](ClO_4)_4$ (**5**) from aqueous solution containing $NaHCO_3$ in a molar ratio of 1:1.

(12) Anal. Calcd for $[Zn_2CO_3(L)](ClO_4)_2\cdot 2H_2O$, $Zn_2Cl_2N_8O_{13}C_{33}H_{66}$: C, 40.26; H, 6.76; N, 11.38. Found: C, 40.05; H, 6.45; N, 11.29. X-ray analysis: $Zn_2Cl_2N_8O_{13}C_{33}H_{66}$, monoclinic, space group $P2_1/c$ (No. 14), a = 13.591(4) Å, b = 18.152(5) Å, c = 18.576(6) Å, β = 107.88(2)°, V = 4361(2) Å^3, and Z = 4. With the use of 3704 unique reflections ($I > 3\sigma(I)$) collected at room temperature with Mo Kα (λ = 0.710 69 Å) radiation up to 2θ = 50.0° on a Rigaku AFC 7S diffractometer, the structure was solved by direct methods (SAPI91) and refined by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms to a final R value of 0.052 (R_w = 0.036).

(13) It has been reported that zinc(II) complexes of cyclam or its analogs similarly take up atmospheric CO_2 in alcohol as alkyl carbonate: Kato, M.; Ito, T. *Inorg. Chem.* **1985**, *24*, 504–508; **1985**, *24*, 509–514.

Scheme I



[a] Main component: $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$.[15] [b] Eluting agent: 0.3 M NaBr aqueous solution.

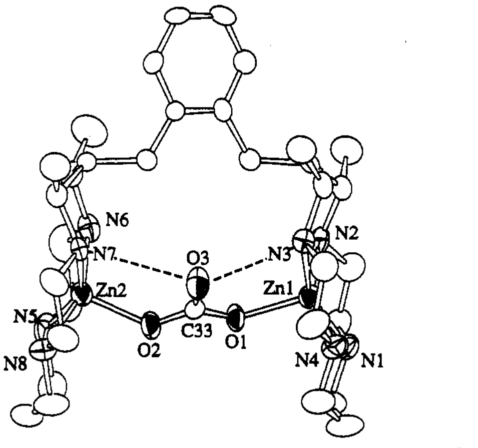


Figure 2. ORTEP drawing of $[Zn_2CO_3(L)]^{2+}$ in **6**. Distances (Å) and angles (deg): Zn(1)–O(1) = 1.978(5), Zn(2)–O(2) = 1.969(5), O(1)–C(33) = 1.285(8), O(2)–C(33) = 1.272(8), O(3)–C(33) = 1.260(8), Zn(1)–N = 2.096(6)–2.127(6), Zn(2)–N = 2.091(6)–2.143(7); O(1)–Zn(1)–N = 98.8(2)–103.8(2), O(2)–Zn(2)–N = 94.7(2)–112.4(2).

and CO_3^{2-} in **6**. The structures of the dinucleating ligand in **3** and **6** are essentially the same.[16] The stereochemistry of the cyclam ring is important in achieving the cofacial ring arrangement. In both compounds, all the cyclam rings adopt the most stable conformation, the so-called "trans-III" type.[17] In each cyclam ring, two methyl groups are disposed at equatorial positions with respect to the chair-form six-membered chelate ring, and thus the combination of chirality of the two asymmetric carbon centers is of meso-type. On the other hand, the xylylene group takes the axial orientation. This fact is important for the cofacial ring arrangement, since two cyclam rings can take the face-to-face arrangement only when the *ortho*-xylylene group adopts the axial orientation. The axial orientation of the xylylene group is undoubtedly caused by the presence of the two methyl groups on the same six-membered ring. In the course of the reduction of the imine bonds in the precursor **2**, the methyl groups in preference to the xylylene group take equatorial positions in the resulting chair-form six-membered ring, thus placing the xylylene group at the axial position.

Since a thermal ellipsoid of the bridging Br(2) in **3** was unusually elongated, it was finally located at two disordered positions related by the C_2 axis. This gave normal thermal ellipsoid and a Ni–Br(2) separation of 2.573(2) Å, which is within the normal coordination bond distance. The Ni–Ni separation is 5.802(2) Å, and the Ni–Br(1) distance is very long [2.881(1) Å]. Each Ni(II) ion is, therefore, in a square-planar four-coordinate geometry at 50% probability and in a five-coordinated square-pyramidal environment at 50%. The magnetic behavior of **3** in the range 3–300 K has been well interpreted with the disordered structure.[18]

In compound **6**, two zinc ions within a molecule are crystallographically independent, but their coordination geometry is very similar and of the square-pyramidal type. The zinc ion is deviated from the best plane comprised of four nitrogen donors of the cyclam ring by 0.425 Å for Zn(1) and 0.445 Å for Zn(2) toward the bridging ligand. The Zn–Zn separation is 5.806(2) Å. The orientation of the CO_3^{2-} group appears to be determined by the hydrogen bonds, which operate between the uncoordinated oxygen of $CO_3^{2-}$and secondary amine protons [O(3)–N(3) = 2.896(8), O(3)–N(7) = 3.193(7) Å].

The present dinucleating ligand (L) forms dimetallic complexes with metal–metal separations of 5.4[15]–5.8 Å when an appropriate bridging ligand connects the bimetallic sites in the cofacial ring arrangement. The metal–metal separation appears to be slightly longer for the Br^- or Cl^- [15] bridge in the dinickel(II) complex. By the combination of metal ions and bridging ligands, a variety of uses of the bimetallic site such as substrate binding in a catalytic process or creation of a new physical property via a metal–metal interaction would be possible with the dinucleating ligand.

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Supplementary Material Available: For **3** and **6**, tables of crystallographic data and experimental conditions, atomic positional and thermal parameters, and interatomic distances and bond angles and figures showing the labeling schemes (19 pages). Ordering information is given on any current masthead page.

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(14) Crystal data: $[Ni_2Br_3(L)]Br \cdot H_2O$, $Ni_2Br_4N_8OC_{32}H_{64}$, monoclinic, space group $C2/c$ (No. 15), $a = 9.233(4)$ Å, $b = 20.865(3)$ Å, $c = 20.945(3)$ Å, $\beta = 95.40(2)°$, $V = 4016(1)$ Å^3, and $Z = 4$. With the use of 1852 unique reflections ($I > 3\sigma(I)$) collected at room temperature with Mo Kα ($\lambda = 0.710\ 69$ Å) radiation up to $2\theta = 49.9°$ on a Rigaku AFC 5S diffractometer, the structure was solved by direct methods (TEXSAN) and refined by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms to an R value of 0.061. In the final least-squares refinement, Br(2) was located at two disordered positions related by the C_2 axis, giving $R = 0.047$ ($R_w = 0.050$) and a normal thermal ellipsoid (see text).

(15) A very similar Cl^- bridged face-to-face ring structure has been found in the crystal structure of $Ni_2(L)Cl_2(ClO_4)_2 \cdot 1.5H_2O$ [Ni–Ni separation is 5.421(3) Å], and magnetic interactions among intra- and intermolecules have been observed. Crystal data: $Ni_2Cl_4N_8O_{9.5}C_{32}H_{65}$, orthorhombic, space group $Ccm2_1$, $a = 20.28(1)$ Å, $b = 21.90(1)$ Å, $c = 19.63(1)$ Å, $V = 8718(1)$ Å^3, $Z = 8$, and $R = 0.065$.

(16) In **3**, a crystallographic C_2 axis bisects C–C bonds in benzene ring and passes through the center of the disordered Br(2) atoms. In **6**, a similar pseudo-C_2 axis can be assumed with respect to the dinucleating ligand structure.

(17) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102–1108.

(18) The magnetic moment of **3** stays constant at 2.9 μ_B over the temperature range 40–300 K. Below 10 K, it goes down sharply toward zero magnetic moment due to the effect of the zero-magnetic-field splitting of Ni(II) ion.